# Thermal Characterization of Polymers

| Polymer | Tg ($^oC$) | Temperature at 10% weight loss ($^oC$/in $N_2$) |
|---|---|---|
| BP-PEPO | 239 | 513 |
| BP-PEPO 10% BFPPO-SNa | 258 | 491 |
| BP-PEPO 20% BFPPO-SNa | 283 | 499 |
| BP-PEPO 30% BFPPO-SNa | 301 | 470 |
| BP-PEPO 50% BFPPO- SNa | 313 | 463 |

# Conclusions

- Standardized procedure for the synthesis and purification of sulfonated BFPPO
- Characterized sulfonated BFPPO
- Prepared high molecular weight BP-PEPO polymers with various degrees of sulfonated BFPPO
- Characterized molecular and thermal properties of these polymers
- As the degree of sulfonated BFPPO was increased, the Tg increased and the intrinsic viscosity increased

# Research Foci

Develop membranes with elevated temperature operations.

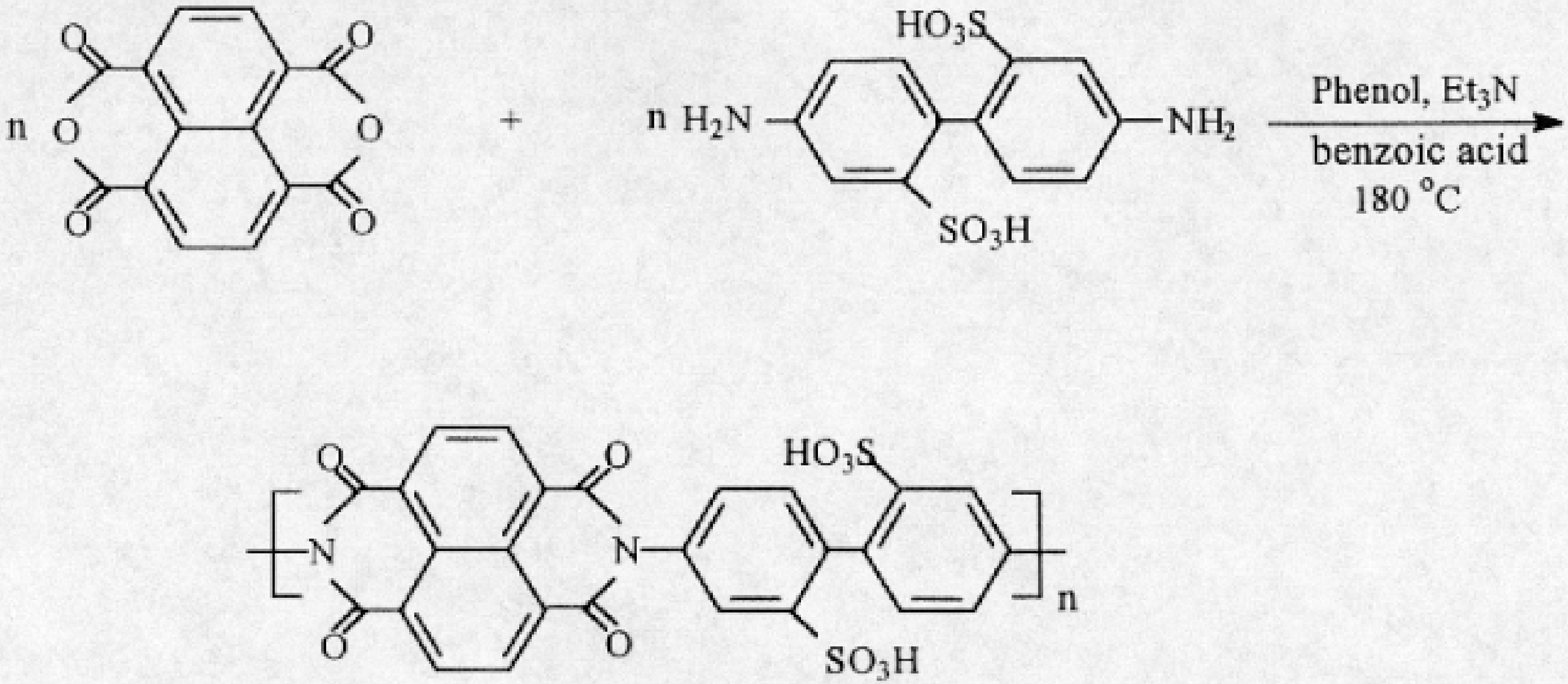
- *Greater than 120°C may allow dramatically increased CO tolerance and direct methanol oxidation rates.*

Improved membrane stability is a key need.

Insights from modeling work on Nafion water systems needed.

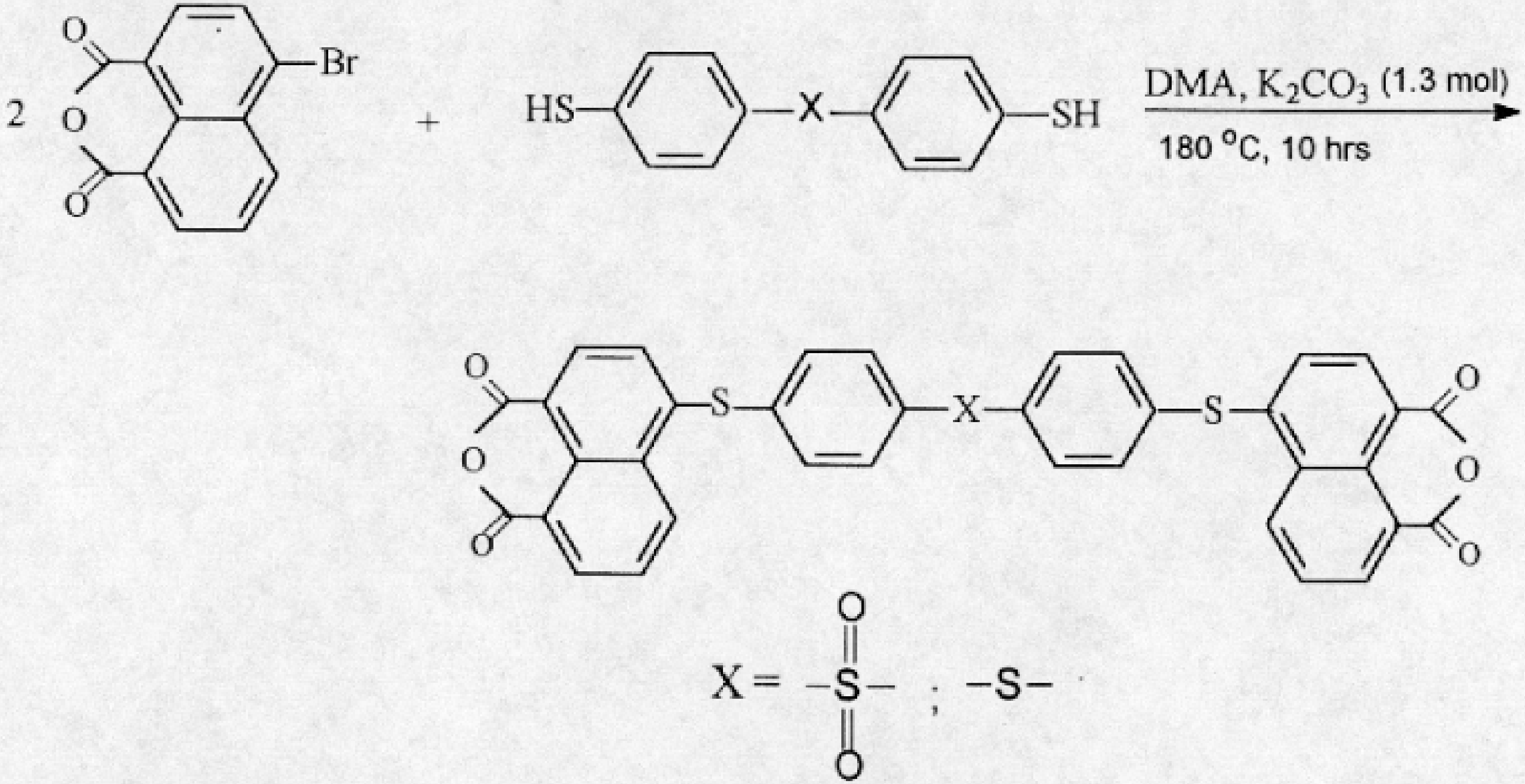
Block ionomeric copolymers.

# General Reaction Scheme for Sulfonated Rigid-Rod PolyNaphthoyleneimide




**Ref.** Timofeeva, G.I., Ponomarev. I.I., Khokhlov, A.R., Mercier, R., Sillion, B. Macromolecular Symp., Nano-Structures and Self Assemblies in Polymer Systems, 1996, 106, 345

# General Reaction Scheme for Preparing Bis-(thioethernaphthalic anhydride) Monomers

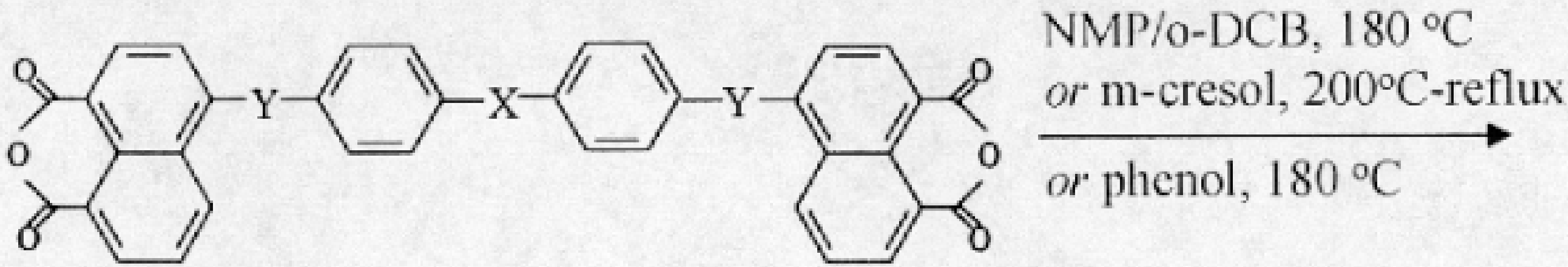


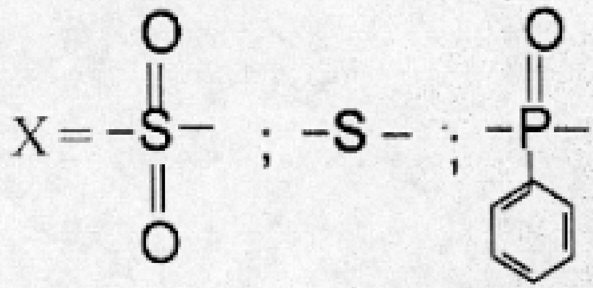

* Precipitated in *i*-propanol

**Ref.** A.L. Rusanov, *Advances in Polymer Sciences*, 111, 115, 1994

# Ongoing and Future Research

Polymer syntheses using bis(naphthalic anhydrides) containing structural fragments



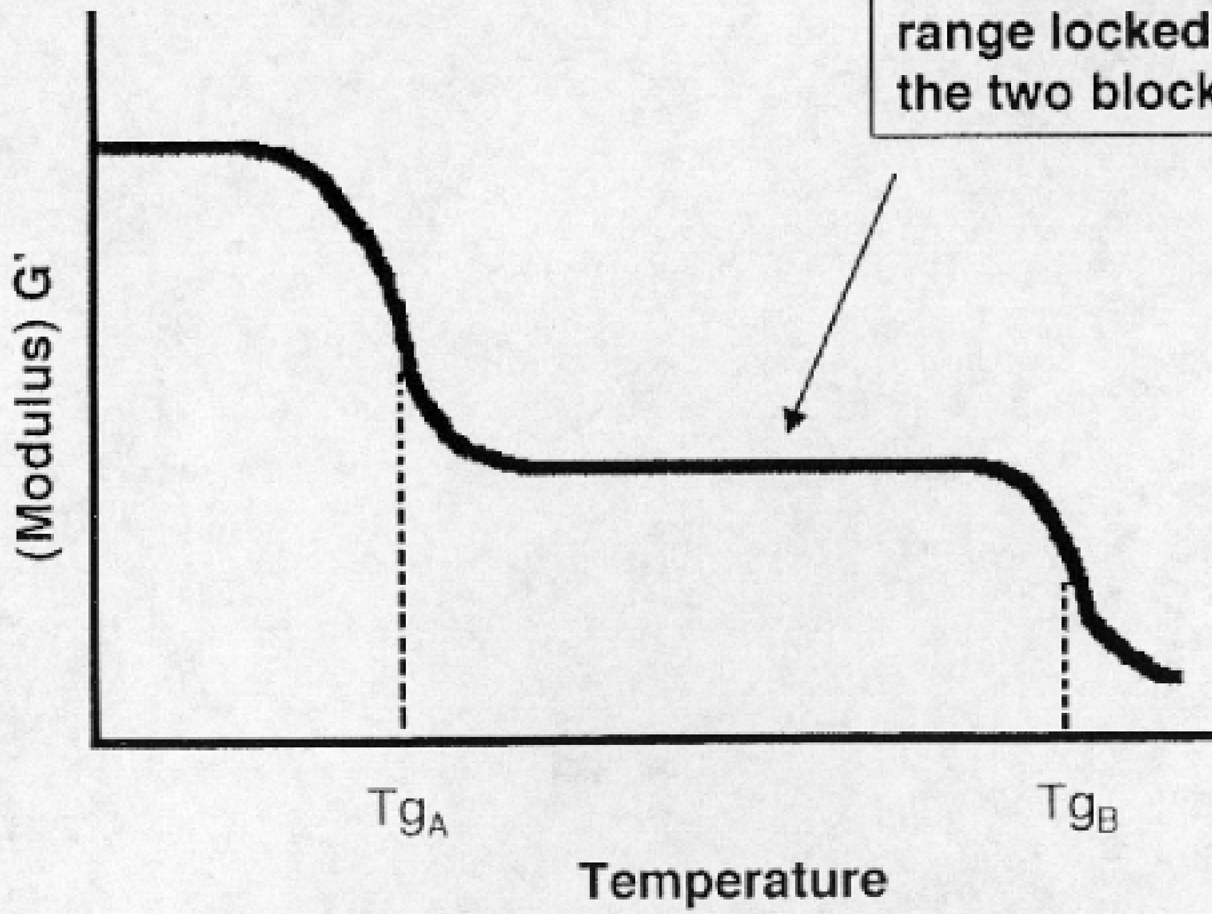




Y = –S– ; –O–

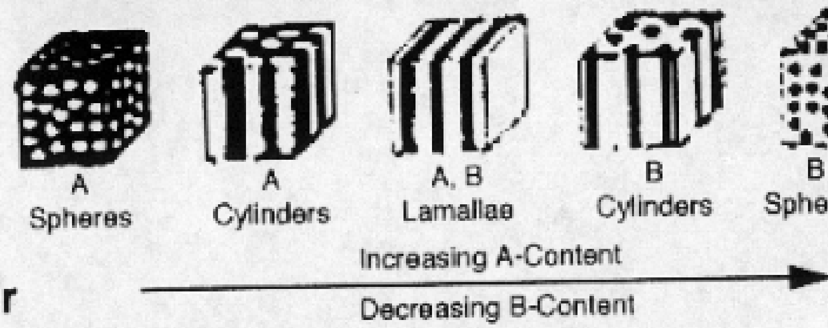
# Modulus-Temperature Behavior of a Block Copolymer

## Multi-Phase

A constant stiffness (flexibility) is achieved within a temperature range locked in by the Tg's of the two blocks.



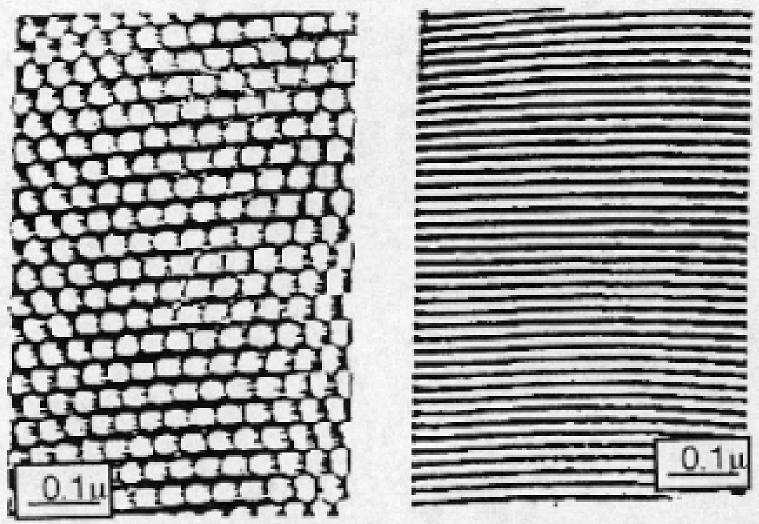
# Morphology vs. Volume Fraction



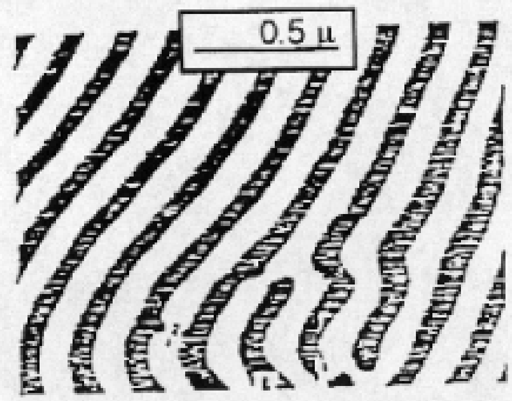

Changes in the morphology of an A-B-A block copolymer as a function of composition.

**Rod- Cylinder**

**Styrene-Isoprene STAR**




Electron Micrographs of SI-DVB-4 star block copolymer. Specimens microtomed in two different directions.




Morphology of styrene-butadiene block copolymers. Configuration of a 60-40 styrene-butadiene diblock copolymer

# Block Copolymers:
# Overview and Critical Survey

Applications for Commercial Block Copolymers

- Elastomers
- Toughened Thermoplastics
- "Surfactants"

Important Parameters and Properties

- Thermal
- Processability
- Mechanical
- Optical
- Chemical Resistance
- Transport
- Surface
- Blending Characteristics

# Objectives

- Develop a phosphotungstic acid impregnated sulfonated poly(arylene ethersulfone/phosphine oxide) proton-exchange membrane with improved conductivity
- Understand the specific interaction among those groups

# Phosphorus Based Solid Acids Increase the Conductivity of Proton Exchange Membrane

- Increase the water uptake
- Increase the protonic conductivity

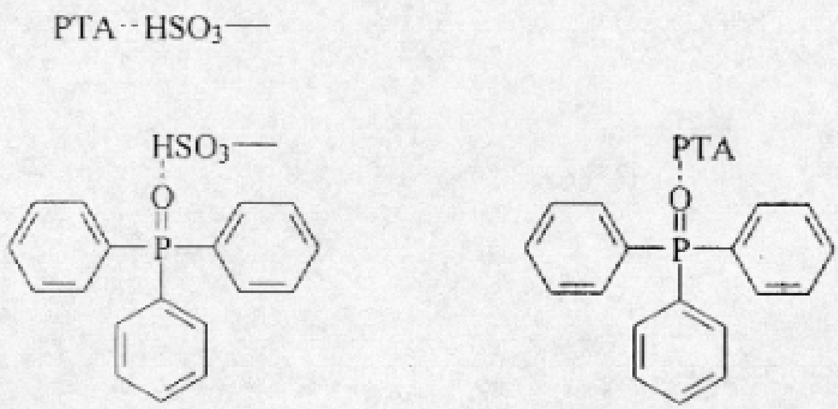

References:

Malhotra, S.; Datta, R. J. *Electrochem. Soc.* , 1997, *144*, L23.

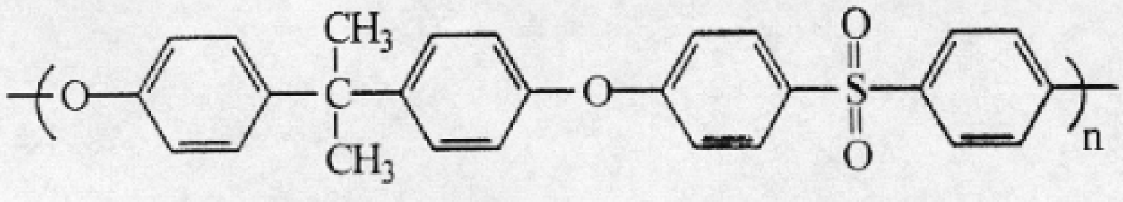
Baradie, B.; Poinsignon, C.; Sanchez, J. Y.; Piffard, Y. *Macromol. Symp.* **1999**, *138*, 85.

# Proposed Approach for the Increase of Conductivity

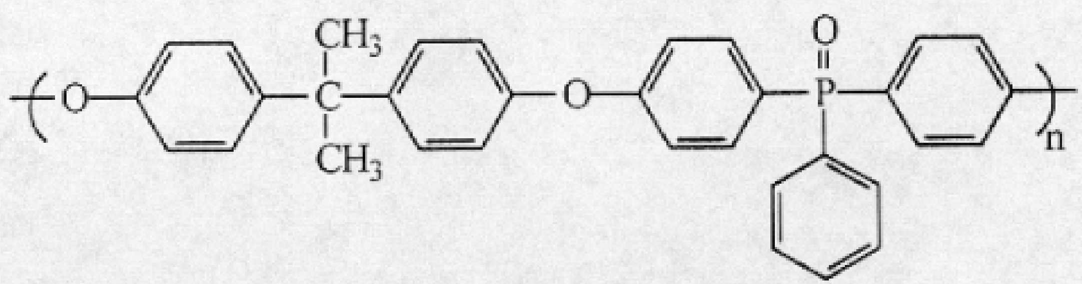
- Hydrogen bonding



# Bisphenol A Poly(Arylene Ether Sulfone) and Bisphenol A Poly(Arylene Ether Phenyl Phosphine Oxide)



Bisphenol A Polysulfone (Udel)



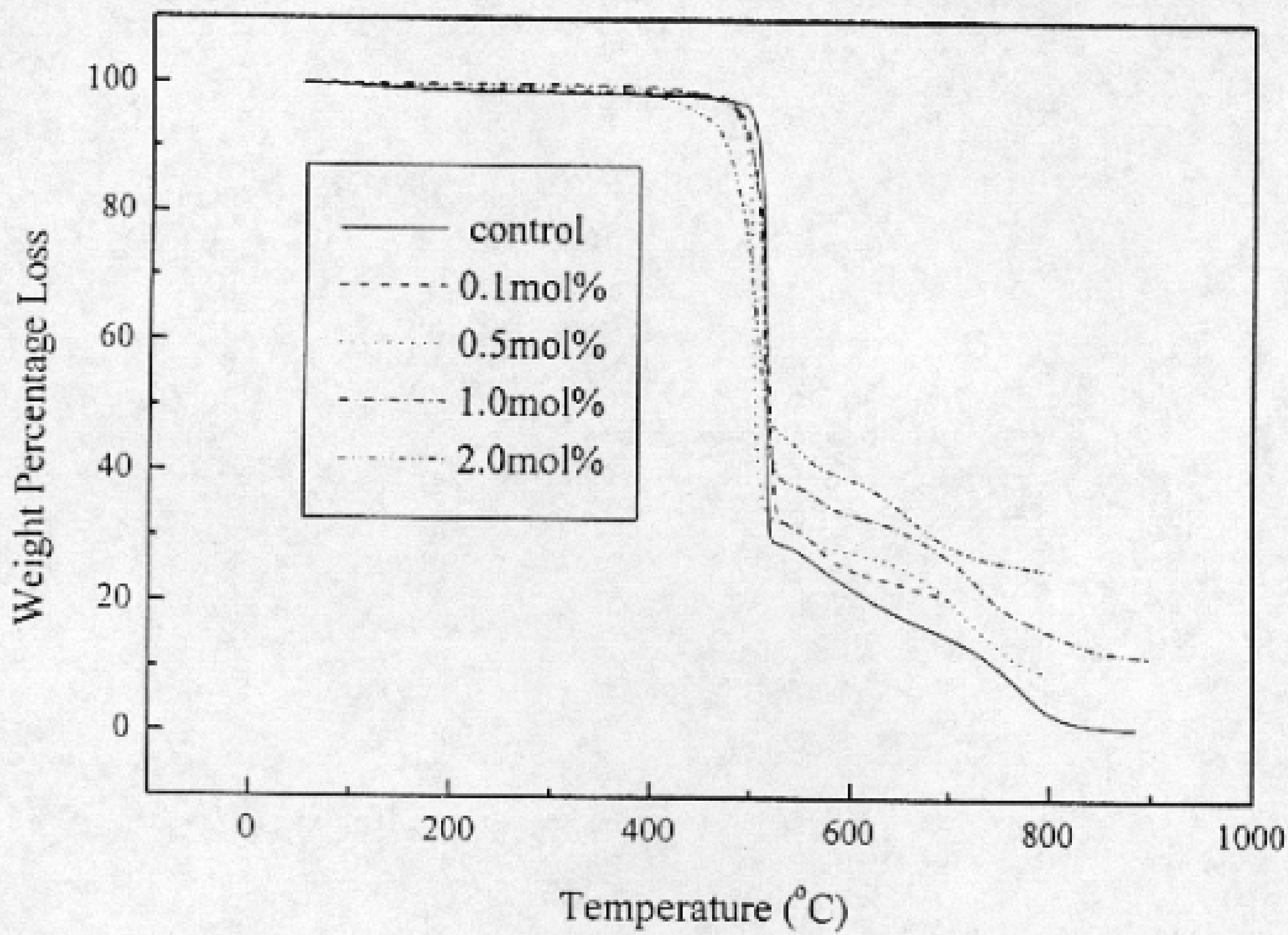
Bisphenol A Poly(arylene ether phenyl phosphine oxide) (BPA PEPO)

BPA PEPO is miscible with phenoxy resin, epoxy resin, and vinyl ester and can afford transparent films with some inorganic salts and silica colloid.

# Film Preparation

- Bisphenol A poly(arylene ether phenyl phosphine oxide) and phosphotungstic acid were dissolved in DMAc with various compositions and stirred for 24 hours. The solutions were cast onto glass plates and dried at about 65°C for overnight. The obtained films were further dried in a vacuum oven for 24 h. As a control bisphenol A polysufone was also used to prepare the films with the same procedure.

# Thermostability of BPA PEPO/PTA
# 10°C/min in air



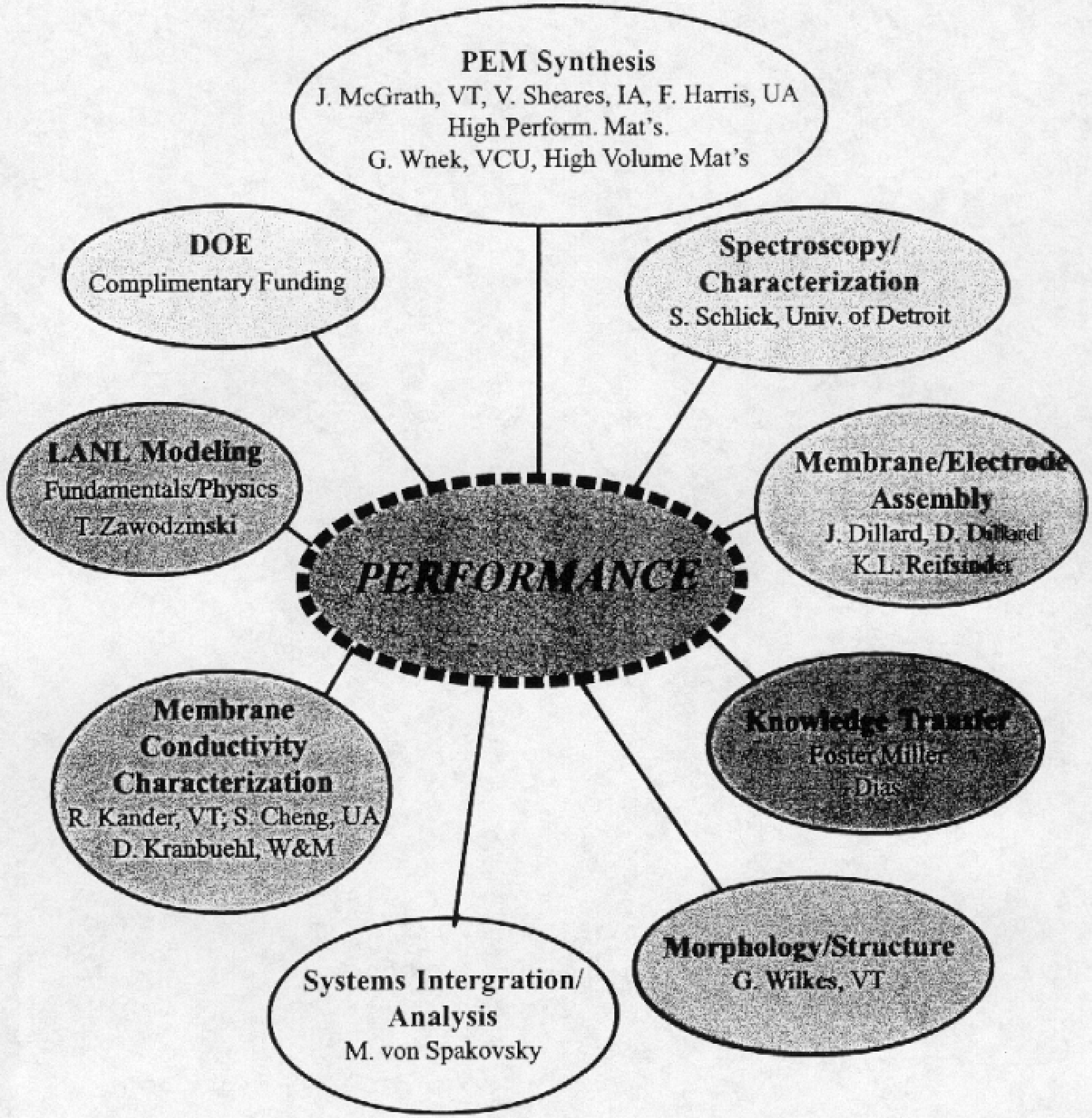
# Conclusions

- BPA PEPO and PTA can be codissolved into DMAc and clear solutions (more than 5 mol%) were obtained.
- Low mol % ( about 0.5 mol%) of PTA can be incorporated into BPA PEPO and transparent films were obtained.
- Udel and PTA were dissolved into DMAc and only turbid solutions were obtained.
- The incorporation of PTA into BPA PEPO does not significantly affect the thermostability.
- The glass transition temperature does not increase with the incorporation of PTA.

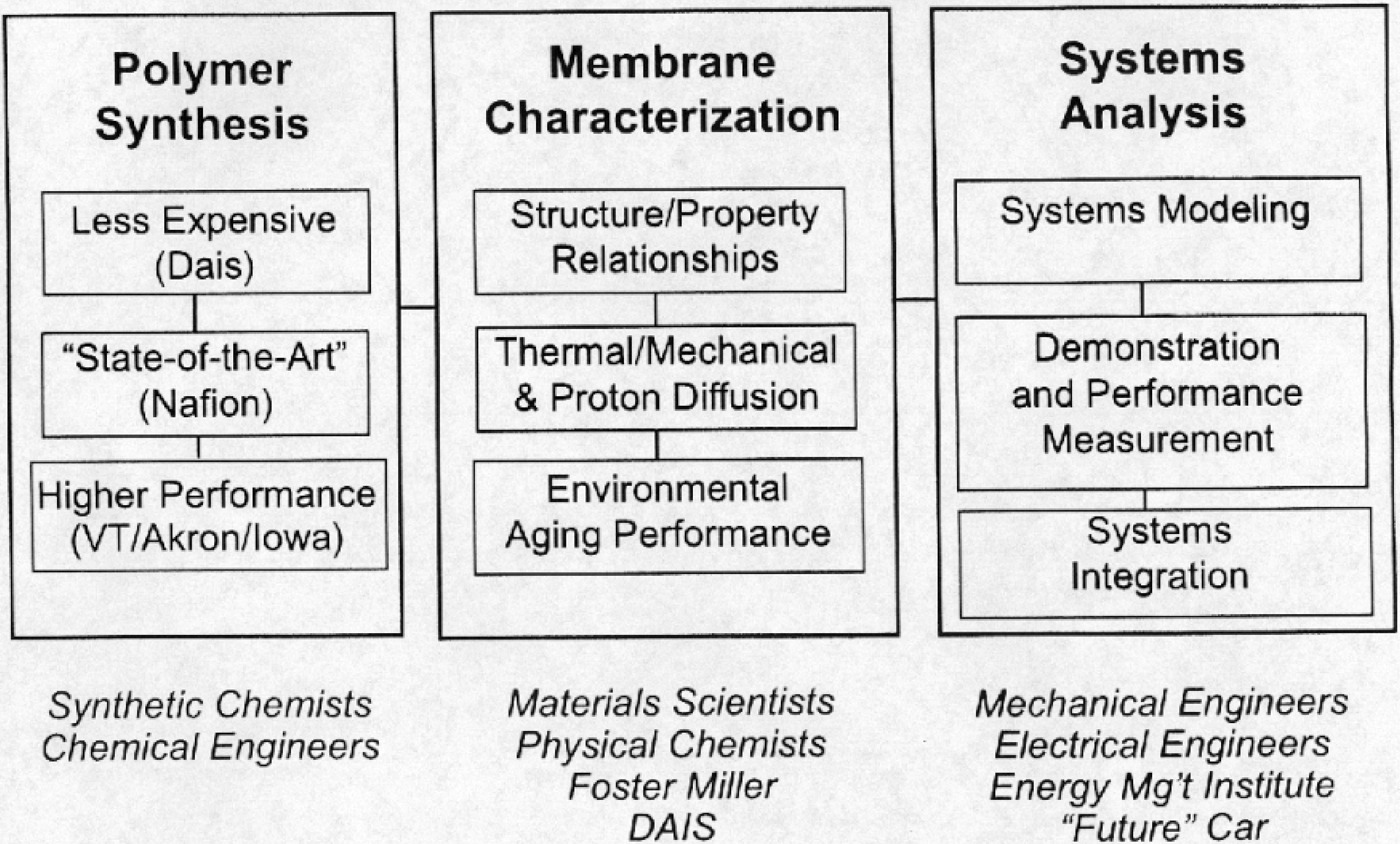
# Future Work

- Model study of the interaction between triphenyl phosphine oxide and sulfonated monomer, triphenyl phosphine oxide and PTA, sulfonated monomer and PTA (PNMR, UV, IR)
- Investigation of those polymers
- Further characterize the physical properties

# A Vision for a Polymeric Electrolyte Proton Exchange Membrane (PEM) Fuel Cell Research IRG



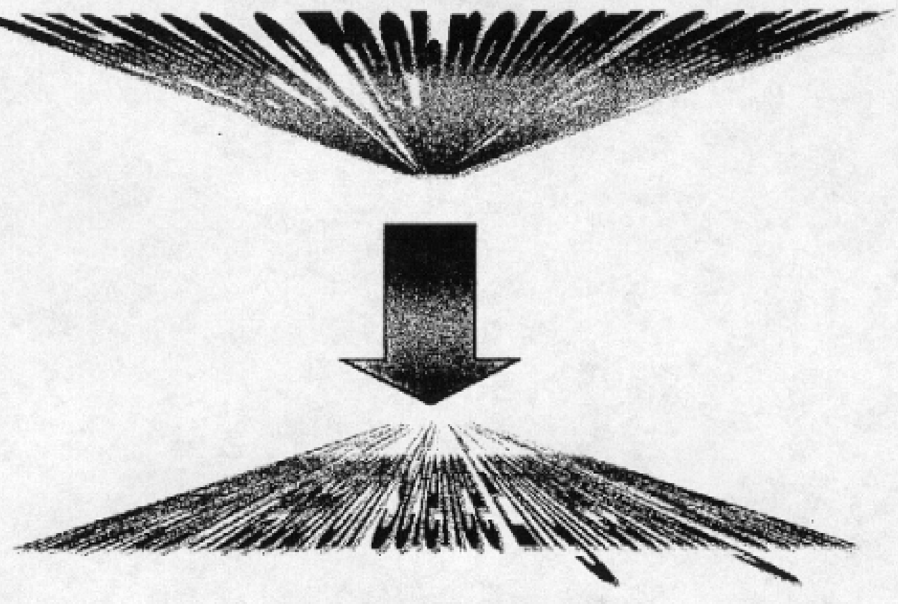
# The Polymeric Electrolyte Proton Exchange Membrane (PEP-EM) will be Multi- and Interdisciplinary



# 1989 . 2000

# Science & Technology Center

Science & Technology Center



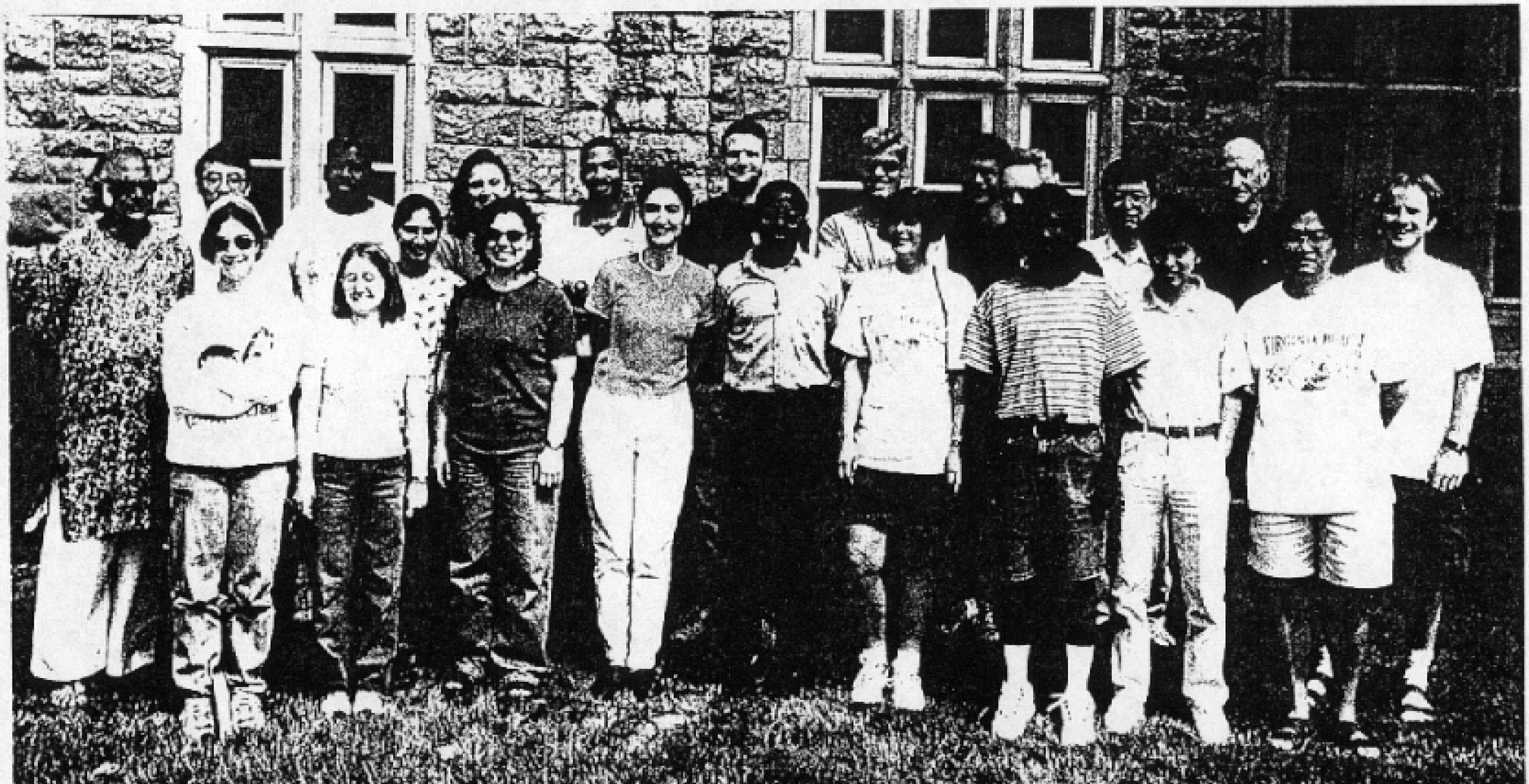
# Materials Research Science Engineering Center

Materials Research Science Engineering Center

# 2000

# Future Collaborations

- Possibility of DOE Programs complimenary to proposed NSF MRSEC effort



Dr. McGrath's 1999 Research Group